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(54) Title: LIQUID CURABLE RESIN COMPOSITION

(57) Abstract

A liquid curable resin composition which exhibits a high curing rate, provides high productivity due to the low viscosity, and can be easily removed from the bound objects. The composition is useful as a bundling material for ribbon materials. The liquid curable resin composition comprises a polyol polyurethane containing an ethylenically unsaturated group, a polyfunctional compound containing three or more (meth)acryloyl groups, and a compound containing N-vinyl groups.

TITLE OF THE INVENTION

LIQUID CURABLE RESIN COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a liquid curable resin composition, and more particularly, to a liquid curable resin composition exhibiting excellent coatability to ribbon matrixes due to the low viscosity, being able to cure fast, and capable of producing cured products with superior tearing characteristics due to the small elongation. The resin composition is suitable for use as a material for bundling ribbon matrixes.

Description of the related art:

In the production of optical fibers, a resin coating is provided for protection and reinforcement immediately after spinning molten glass fibers. A known structure of the resin coating consists of a primary coating layer of a flexible resin which is coated on the surface of optical fibers and a secondary coating layer of a rigid resin which is provided over the primary coating layer. A so-called optical fiber ribbon is known in the art in the application of coated optical fibers. The optical fiber ribbon is made from several elemental optical fibers, e.g. four or eight optical fibers, by arranging these fibers in a plane and fixing them with a binder to produce a ribbon structure with a rectangular cross section. A multiple core ribbon structure prepared by binding two or more optical fiber ribbons, for example, a ribbon structure made from eight elemental fibers consisting of two

ribbons, each made from four elemental optical fibers bound together, is also known. The resin compositions for coating these optical fibers include a soft material used for producing the primary coating layer, a hard material used for producing the secondary coating layer, a ribbon matrix material for preparing optical fiber ribbons from several optical fibers, and a bundling material for producing multiple core ribbon structure consisting of several optical fiber ribbons.

The characteristics required for curable resins used as the bundling materials for optical fibers include: to be curable fast, to have a sufficient low viscosity to be coated to ribbon materials at a high speed, thereby providing excellent productivity, and to produce cured products with sufficient strength and superior flexibility, exhibiting very little physical change during temperature changes over a wide range, showing superior long term reliability with little physical changes over time, showing superior resistance to chemicals such as acids and alkalis, exhibiting low moisture and water absorption, and exhibiting superior surface characteristics and having a small coefficient of friction. The characteristics of a bundling material to be comparatively easily released and separated from materials which are bound by this bundling material are demanded of the bundling materials not only used with optical fibers, but also used for other purposes. Such characteristics are demanded particularly in the cases where temporary or semi-eternal bundling is required, such as the case where two structural materials are temporarily bound when these are attached or welded together or the case where several parts are temporarily bound until these are delivered to consumers.

SUMMARY OF THE INVENTION

An object of the present invention is therefore to provide a liquid curable resin composition, and particularly a liquid curable resin composition which can be rapidly cured, exhibits high productivity due to the low viscosity, and easily separated from articles which are bound by this resin composition without leaving adhered residue after separation.

This object can be solved by the present invention by a liquid curable resin composition comprising (A) a polyol polyurethane containing an ethylenically unsaturated group, (B) a polyfunctional compound containing three or more (meth)acryloyl groups, and (C) a compound containing N-vinyl groups in a proportion of 0.25 to 2 mols for one mol of the (meth)acryloyl group contained in the composition.

Other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

(A) Polyol polyurethane containing an ethylenically unsaturated group

The polyol polyurethane containing ethylenically unsaturated group (Component (A)) used in the present invention can be prepared by reacting a polyol, a diisocyanate, and a compound having an ethylenically unsaturated group, specifically, by reacting the isocyanate group of the diisocyanate with the hydroxyl group of the polyol and the compound having an ethylenically unsaturated group.

The reaction can be carried out, for example, by the following methods: a method of simultaneously reacting the polyol, the diisocyanate, and the compound having an ethylenically unsaturated group; a method of

reacting the polyol and the diisocyanate to obtain an intermediate compound, and reacting this intermediate compound with the compound having an ethylenically unsaturated group; a method of reacting the diisocyanate and the compound with an ethylenically unsaturated group, and then reacting the resulting compound with the polyol; a method of reacting the diisocyanate and the compound with an ethylenically unsaturated group, reacting the resulting compound with the polyol, then again reacting with the compound with an ethylenically unsaturated group.

Examples which can be given of the polyol used in these reactions include aliphatic polyether diols, alicyclic polyether diols, aromatic polyether diols, polyester diols, polycarbonate diols, polycaprolactone diols, and other polyols. These polyols may be used either individually or in combinations of two or more. The manner of polymerization of each constitutional unit in these polyols is not specifically limited and may be random polymerization, block polymerization, or graft polymerization.

Given as examples of aliphatic polyether diols among these polyols are polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether diols obtained by the ring-opening copolymerization of two or more ionic-polymerizable cyclic compounds.

Examples of the ionic-polymerizable cyclic compound include cyclic ethers such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, 3,3'-bischloromethyloxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrine, glycidyl methacrylate, allyl glycidyl ether, allyl glycidyl carbonate,

butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidylbenzoate.

Specific examples of the polyether diol obtained by the ring-opening copolymerization of two or more types of these ionic-polymerizable cyclic compounds include binary copolymers and ternary copolymers, specifically, binary copolymers such as those obtained by the combination of tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyltetrahydrofuran, tetrahydrofuran and ethylene oxide, propylene oxide and ethylene oxide, and butene-1-oxide and ethylene oxide; and ternary copolymers obtained by the combination of tetrahydrofuran, butene-1-oxide, and ethylene oxide.

It is also possible to use a polyether diol obtained by the ring-opening copolymerization of one of the above-mentioned ionic-polymerizable cyclic compounds and a cyclic imine such as ethylene imine, a cyclic lactone such as β-propiolactone and glycolic acid lactide, or a cyclic siloxane such as dimethylcyclopolysiloxane.

The above-mentioned aliphatic polether diols are commercially available under the trademarks, for example, of PTMG 650, PTMG 1000, PTMG 2000 (Mitsubishi Chemical Corp.); PPG 400, PPG 1000, EXCENOL 720, EXCENOL 1020, 2020, (Asahi Oline Co., Ltd.); PEG 1000, UNISAFE DC 1100, UNISAFE DC 1800 (Nippon Oil and Fats Co., Ltd.); PPTG 2000, PPTG 1000, PTG 400, PTGL 2000 (Hodogaya Chemical Co., Ltd.); and Z-3001-4, Z-3001-5, PBG 2000A, PBG 2000B, EO/BO 4000, EO/BO 2000 (Daiichi Kogyo Seiyaku Co., Ltd.).

Alkylene oxide adducts to hydrogenated bisphenol A, alkylene oxide adducts to hydrogenated bisphenol F, and alkylene oxide adducts to 1,4-

cyclohexane diol are given as examples of alicyclic polyether diol.

Alkylene oxide addition diol to bisphenol A such as polyoxyethylene bisphenol A ether, alkylene oxide addition diol to bisphenol F, alkylene oxide addition diol to hydroquinone, alkylene oxide addition diol to naphthohydroquinone, and alkylene oxide addition diol to anthrahydroquinone are given as examples of aromatic polyether diols. The aromatic polyether diols are also commercially available under the trademarks, for example, of Uniol DA400, DA700, DA1000, and DA4000 (Nippon Oil and Fats Co., Ltd.).

Polyester diols obtained by the reaction of a polyhydric alcohol and a polyacidic base are given as examples of the polyester diol. Ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, 3-methyl-1,5-pentane diol, 1,9-nonane diol, and 2-methyl-1,8-octane diol, are given as examples of the polyhydric alcohol. As examples of the polyacidic base, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, and sebacic acid can be given. Commercially available polyester diols which can be used include, for example, Kurapol P-2010, PMIPA, PKA-A, PKA-A2, PNA-2000 (Kuraray Co., Ltd.).

A polycarbonate of polytetrahydrofuran and a polycarbonate of 1,6-hexane diol can be given as examples of the polycarbonate. The polycarbonate can also be commercially available under the trademarks, for example, of DN-980, DN-981, DN-982, DN-983 (Nippon Polyurethane Industry Co., Ltd.), PC-8000 (PPG of the US), and PC-THF-CD (BASF).

Given as examples of the polycaprolactone diol are polycaprolactone diols obtained by the reaction of ϵ-caprolactone and a diol. Such a diol may

be, for example, ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, and 1,4-butane diol. These polycaprolactone diols can be also commercially available under the trademarks such as PLACCEL 205, 205AL, 212, 212AL, 220, 220AL (Daicel Chemical Industries, Ltd.).

Other polyol compounds which can be used include dimethylol compounds of ethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, hydrogenated bisphenol A, hydrogenated bisphenol F, or dicyclopentadiene; tricyclodecane dimethanol, pentacyclopentadecane dimethanol, ß-methyl-δ-valerolactone, polybutadiene with terminal hydroxyl groups, hydrogenated polybutadiene with terminal hydroxyl groups, castor oil modified polyol, polydimethylsiloxane with terminal diols, and polydimethylsiloxane carbitol-modified polyols.

The number average molecular weight of the polyol for producing component (A) is usually 50-15,000, and preferably 100-12,000.

Among polyether polyols, polyester polyols, polycarbonate polyols, and polycaprolactone polyols, the polyether polyols can produce polyurethane with particularly excellent durability and low-temperature characteristics.

Given as examples of the diisocyanates used for producing component (A) of the present invention are 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene diisocyanate,

4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, bis(2-isocyanate-ethyl) fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, lysine diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, and tetramethylxylylene diisocyanate. Among these diisocyanates, 2,4-tolylene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, and methylenebis(4-cyclohexylisocyanate) are particularly preferred.

These diisocyanates may be used either individually or in combinations of two or more.

Examples of the compounds having an ethylenically unsaturated group used for producing the component (A) include (meth)acrylates containing a hydroxyl group, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxyalkyl(meth)acryloyl phosphate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, (meth)acrylates represented by the following structural formulas (1) or (2),

$$CH_2{=}C(R^1)\text{-}COOCH_2CH_2\text{-}(OCOCH_2CH_2CH_2CH_2CH_2)_n\text{-}OH \qquad (1)$$

$$CH_2{=}C(R^1)\text{-}COOCH_2CH(OH)CH_2\text{-}O\text{-}(C_6H_5) \qquad (2)$$

wherein R^1 is a hydrogen atom or a methyl group and n denotes an integer of 1-15. Among these (meth)acrylates having a hydroxyl group, particularly desirable are 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl

(meth)acrylate. Besides these compounds, compounds obtained by the addition reaction of a compound containing a glycidyl group, such as, alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and (meth)acrylic acid can also be used as the compound having an ethylenically unsaturated group.

These compounds having an ethylenically unsaturated group may be used either individually or in combination of two or more.

The proportion of the polyol, the diisocyanate, and the compound having an ethylenically unsaturated group used for preparing the component (A) is such that for one mol of the hydroxyl group of the polyol, 1.1-3 mols of the diisocyanate group contained in the diisocyanate compounds and 0.2-1.5 mols of the hydroxyl group contained in the hydroxyl group-containing (meth)acrylate are used. A particularly preferred proportion is for one mol of the hydroxyl group of the polyol, 1.5-2 mols of the diisocyanate group contained in the diisocyanate compounds and 0.5-1.0 mols of the hydroxyl group contained in the hydroxyl group-containing (meth)acrylate.

In the above reaction, a urethanization catalyst such as copper naphthenate, cobalt naphthenate, zinc naphthenate, di-n-butyl-tin-laurylate, triethylamine, 1,4-diazabicyclo[2.2.2]-octane, or 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane is used, generally, in an amount of 0.01 to 1 part by weight for 100 parts by weight of the reaction raw materials. The reaction temperature is normally in the range of 10-90°C, preferably of 30-80°C.

The component (A) has a weight average molecular weight reduced to polystyrene of 500 to 20,000. If the weight average molecular weight is less than 500, flexibility of the cured product may be

reduced due to a small molecular weight between cross-linking points and deformation due to shrinkage during curing may increase. If the molecular weight is larger than 20,000, on the other hand, the strength of the resin after cure may be insufficient.

The component (A) is incorporated in the composition in an amount preferably of 10-90% by weight, and more preferably 20-80% by weight.

(B) Polyfunctional compound containing three or more (meth)acryloyl groups

The polyfunctional compound (B) contains three or more (meth)acrylate groups. Generally, the compound (B) will contain less than 10 (meth)acrylate groups, preferably less than 6. The molecular weight is not critical, and will generally be between 300-2000. Preferably, the molecular weight is less than 1000.

Given as examples of the polyfunctional compound containing three or more (meth)acryloyl groups used as the component (B) in the present invention are trimethylolpropane tri(meth)acrylate, ethoxylated trimethylolpropane tri(meth)acrylate, propoxylated trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, dipentaerythritol monohyroxypenta(meth)acrylate, tris(2-(meth)acryloxyethyl)-isocyanurate tri(meth)acrylate, and the like.

The component (B) can also be commercially available under the trademarks, for example, of FA731A (Hitachi Chemical Co., Ltd.); ARONIX M-315, M-350, M-360, M-405, M-450 (Toagosei Chemical Industry Co., Ltd.); KAYARAD DPHA, D-310, D-320, D-330, DPCA-20, DPCA-30, DPCA-60, DPCA-120 (Nippon Kayaku Co., Ltd.); and Viscoat 400 (Osaka Organic Chemical Industry,

Ltd.); and Photomer 4172, 4149 (Sun Nopco Co., Ltd.). Of these, ARONIX M-450, Viscoat 400, and Photomer 4149 are preferred.

The component (B) is incorporated in the composition in an amount preferably of 3-75% by weight, and more preferably 5-68% by weight. If less than 3% by weight, not only hardness of the cured products obtained from the resin composition is decreased, but also the rubbery elasticity is increased, resulting in difficulty in separating two bundled optical fiber ribbons due to elongation of the bundling material, when the composition is used as the bundling material for optical fiber ribbons. If the proportion of the component (B) is larger than 75% by weight, on the other hand, hardness of the cured products obtained from the resin composition is unduly increased, so that the bundling material is difficult to be broken and the resin composition exhibits too large shrinkage when cured. Adhesion to optical fiber ribbons is also impaired.

(C) Compound having N-vinyl group

The compound (C) having a N-vinyl group may have one or more N-vinyl groups. Preferably, compound C has one N-vinyl group. Generally, the molecular weight of compound (C) will be higher than 70, and generally lower than 1000. Preferably, the molecular weight and the viscosity of compound (C) are low, so compound (C) acts as a reactve diluent.

Suitable N-vinyl group comprising compounds include N-vinyl pyrrolidone, N-vinyl-carbazole, N-vinyl caprolactam, N-vinyl-formamide and reaction products of N-vinylformamide with e.g. isocyanate comprising compounds.

N-Vinyl pyrrolidone, N-vinyl caprolactam, and the like are preferred examples of the compound having an N-vinyl group used as the component (C).

The amount of the compound having N-vinyl group is such that the proportion of the N-vinyl group is 0.25 to 2 mols for 1 mol of the (meth)acryloyl group contained in the composition. Preferably, the ratio is 0.35 or higher. It is also preferred to have less than 1 mole of N-vinyl group relative to the (meth)acryl group. Either too large or too small an amount of the N-vinyl group for the (meth)acryloyl group in the composition may result in a retarded curing rate due to decrease in the alternate copolymerization of N-vinyl group and (meth)acryloyl group.

Besides the above components (A), (B) and (C), the composition of the present invention preferably comprises other consituents.

A suitable additional compound is a urethane (meth)acrylate compound produced by reacting 2 mols of a (meth)acrylate containing a hydroxyl group and one mol of diisocyanate can be added to the liquid curable resin composition of the present invention. Given as examples of such urethane (meth)acrylates are a reaction product of hydroxyethyl (meth)acrylate and 2,5-bis(isocyanate methyl)-bicyclo[2.2.1]heptane, a reaction product of hydroxyethyl (meth)acrylate and 2,6-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, a reaction product of hydroxyethyl (meth)acrylate and 2,4-tolylene diisocyanate, a reaction product of hydroxyethyl (meth)acrylate and isophorone diisocyanate, a reaction product of hydroxypropyl (meth)acrylate and 2,4-tolylene diisocyanate, a reaction product of hydroxypropyl (meth)acrylate and isophorone diisocyanate. These urethane (meth)acrylate can be used in an amount preferably of 30 parts by weight or less for 100 parts by weight of the total amount of the polyol polyurethane (A) having an ethylenically unsaturated group and urethane (meth)acrylate.

The liquid curable resin composition of the

present invention can be cured by heat or radiation. The composition of the present invention usually contains a polymerization initiator. A heat sensitive polymerization initiator and/or ligt sensitive polymerization initiator can be used as polymerization initiator. Radiation here means radiation such as infrared light, visible light, ultraviolet light, X-rays, electron beams, α-rays, β-rays, and γ-rays.

Preferably, ultraviolet light and/or visible light are used to cure the composition of the present invention.

When the liquid curable resin composition of the present invention is cured by heat, a peroxide or an azo compound is usually used as a heat sensitive polymerization initiator. Benzoyl peroxide, t-butyloxybenzoate, and azobisisobutylonitrile are given as specific examples.

When the liquid curable resin composition of the present invention is cured by radiation, a radiation sensitive polymerization initiator is used. Suitable examples of the radiation polymerization initiator include 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropane-1-one, 2-hydroxy-2-methyl-1-phenylpropane-1-one, thioxanthone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propane-1-one, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide; and commercially available products, such as Irgacure 184, 369, 651, 500, 907, CGI1700, CGI1750, CGI1850,

CG24-61 (Ciba Geigy), Lucirin LR8728 (BASF), Darocure 1116, 1173 (Merck Co.), and Ubecryl P36 (UCB).

When the liquid curable resin composition of the present invention is cured by heat and radiation, the above-described heat polymerization initiators and radiation polymerization initiators may be used together. The polymerization initiators are used in an amount of 0.1-10% by weight, preferably 0.5-7% by weight, in the composition.

Furthermore, other diluents and additives may be used in the liquid curable resin composition of the present invention to the extent that the effects of the present invention are not adversely affected.

Monomers containing (meth)acryloyl group or vinyl group other than the above-described monomers (B) and (C) can be used as a reactive diluent in the coating composition. Such monomers include mono-functional and di-functional monomers.

Given as examples of the mono-functional monomers are alicyclic (meth)acrylates, such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, cyclohexyl (meth)acrylate; (meth)acryloyl group-containing monomers, such as benzyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate, (meth)acryloyl morpholine, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl

(meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, polyoxyethylenenonyl phenyl ether (meth)acrylate, phenoxyethyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acrylate, diacetone (meth)acrylamide, isobutoxymethyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate, N,N-diethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, acryloylmorpholine, and compounds represented by the following formulas (3) to (5).

$$CH_2=C(R^2)-COO(R^3O)_m-R^4 \qquad (3)$$

wherein R^2 is a hydrogen atom or a methyl group; R^3 is an alkylene group containing 2 to 6, preferably 2 to 4 carbon atoms; R^4 is a hydrogen atom or an alkyl group containing 1 to 12, preferably 1 to 9, carbon atoms; and m is an integer from 0 to 12, and preferably from 1 to 8.

$$CH_2 = C(R^2)-COO(R^5O)_p-O-CH_2-R^6 \qquad (4)$$

wherein R^2 is the same as defined in formual (3); R^5 is an alkylene group containing 2 to 8, preferably 2 to 5, carbon atoms; R^6 is a tetrahydrofuryl group; and p is an integer from 1 to 8, and preferably from 1 to 4.

$$CH_2 = C(R^2)\text{-}COO(R^5O)_p\text{-}R^7 \quad (5)$$

wherein R^2, R^5, and p are the same as defined in the formula (4); and R^7 is an aromatic group, preferably a phenyl group, optionally substituted with an alkyl group having 1-18 carbon atoms, preferably 1-9 carbon atoms; and monomers containing a vinyl group other than N-vinyl group, such as hydroxybutyl vinyl ether, lauryl vinyl ether, cetyl vinyl ether, and 2-ethylhexyl vinyl ether. These monofunctional groups can also be commercially available under the trademarks of ARONIX M-111, M-113, M-114, M-117 (Toagosei Chemical Industry Co., Ltd.), KAYARAD TC110S, R629, R644 (Nippon Kayaku Co., Ltd.), and IBXA (Osaka Organic Chemical Industry, Ltd.).

Examples of the di-functional monomers include monomers containing (meth)acryloyl group such as ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, di(meth)acrylate of a diol which is an ethylene oxide adduct to bisphenol A, di(meth)acrylate of a diol which is an ethylene oxide adduct to hydrogenated bisphenol A, and epoxy (meth)acrylate which is a (meth)acrylate adduct to diglycidyl ether of bisphenol A; and vinyl group-containing monomers such as triethylene glycol divinyl ether.

Given as commercially available di-functional monomers are YUPIMER-UV, SA1002 (Mitsubishi Chemical Corp.), Viscoat 700 (Osaka Organic Chemical Industry Ltd.), KAYARAD R-604, HX-620 (Nippon Kayaku Co., Ltd.), and ARONIX M-210, M-215 (Toagosei Chemical Industry Co., Ltd.). Among these di-functional monomers, tricyclodecanediyldimethyl di(meth)acrylate and

diacrylate of a diol which is an alkylene oxide adduct to bisphenol A are particularly preferred.

These reactive diluents may be added either individually or in combinations of two or more to the composition of the present invention in an amount, usually, of 1-80% by weight, preferably 10 to 70% by weight. The addition of the reaction diluents in the amount in this range suitably controls the coatability and curing rate of the resin composition, toughness of the cured products, and reduces shrinkage during cure.

Furthermore, amines may be added to the liquid curable resin composition of the present invention to suppress generation of hydrogen gas which causes a transmission loss of optical fibers. The amines which can be added include diarylamine, diisopropylamine, diethylamine, and diethylhexylamine.

Beside these additives, various other additives may be added as required, such as antioxidants, UV absorbers, photo-stabilizers, silane coupling agents, thermal polymerization inhibitors, leveling agents, surfactants, preservatives, plasticizers, lubricants, coloring agents, solvents, fillers, anti-oxidants, wettability improvers, and coatability improvers.

Commercially available antioxidants which can be used are Irganox 1010, 1035, 1076, 1222 (Ciba Geigy), Antigen P, 3C, FR, GA-80 (Sumitomo Chemical Industries Co., Ltd.), and the like. As UV absorbers, Tinuvin P, 234, 320, 326, 327, 328, 329, 213 (Ciba Geigy), Seesorb 102, 103, 501, 202, 712, 704 (manufactured by Shipro Kasei Co.) can be given. Commercially available photo-stabilizers which can be added include Tinuvin 292, 144, 622LD (manufactured by Ciba Geigy), Sanol LS770 (manufactured by Sankyo Chemical Co.), and SUMISORB TM-061 (manufactured by Sumitomo Chemical Industries). Examples of silane coupling agents which can be given are γ-aminopropyl-

triethoxy silane, γ-mercaptopropyltrimethoxy silane, γ-methacryloxypropyltrimethoxy silane, and commercially available products such as SH6062, SH6030 (Toray Silicone Co.) and KBE903, KBE603, KBE403 (Shin-etsu Chemical Co.).

The viscosity of the liquid curable resin composition of the present invention is normally in the range of 200 to 10,000 cp at 25°C, and preferably 1,000 to 8,000 cp at 25°C.

The liquid curable resin composition of the present invention preferably is used as bundling material in a construction to bind at least two ribbons comprising each at least two coated optical glass fibers bonded by a ribbon matrix material. The coated optical glass fibers preferably are color coated, either by a thin UV-curable ink, or by coloring the secondary coating.

Generally, the bundle of ribbons will comprise 2-20 ribbons, preferably 2-10. The ribbons generally will comprise 2-20 coated optical fibers, preferably 2-12.

It is desirable, that the cured resin composition of the present invention has a Young's modulus of 5-50 kg/mm^2.

It is furthermore desirable, that the cured resin composition has an elongation at break of 70% or lower, preferably 50% or lower. The elongation at break generally will be higher than 3%, and preferably is higher than 10%.

The breaking strength of the cured composition preferably is higher than 0.5 kg/mm^2, and more preferably higher than 1 kg/mm^2. Generally, the breaking strength will be less than 10 kg/mm^2, preferably less than 5 kg/mm^2.

It is desirable that the cured resin composition of the present invention has an adhesion to a ribbon matrix material in the range of 5 to 200 g/cm.

If the adhesion to the ribbon matrix material is too large, it is difficult to peel off the parts of bundling material to be removed, resulting in decrease in processability. If this adhesion is too small, there may be a risk that the parts which should not be removed may also be peeled off.

The present invention will be hereinafter described in more detail by way of examples which are given for illustration of the present invention shall not to be construed as limiting the present invention.

EXAMPLES

Example 1

10408 g of EO/BO 4000 with a number average molecular weight of 4,125 (manyfactured by Daiichi Kogyo Seiyaku Co., Ltd.) as a diol, 713 g of 2,4-tolylene diisocyanate, 2.8 g of 2,6-di-t-butyl-4-methylphenol, as a polymerization inhibitor, and 0.9 g of phenothiazine were charged into a reaction vessel equipped with a stirrer. The mixture was cooled over an ice water bath to 10°C and 9.3 g of dibutyl tin dilaurate was added while controlling the temperature at 20°C or lower. The mixture was stirred for one hour at 10-20°C, and for a further one hour at 50-60°C. Then, 366 g of 2-hydroxyethyl acrylate was added 60°C, followed by stirring for a further 5 hours at 50-60°C, whereupon the reaction was terminated, thereby producing 11,500 g of a polyol polyurethane.

To this were added 3,680 g of tricyclodecanedimethanol diacrylate, 1,610 g of isobornyl acrylate, and 3,450 g of N-vinyl caprolactam, as reactive diluents, 2,300 g of pentaerythritol tetraacrylate as the component (B), 253 g of Lucirin LR872 (manufactured by BASF) and 230 g of Irgacure 907 (manufactured by Ciba Geigy) as photopolymerization initiators. The mixture was stirred for 3 hours at 45 to 55°C thus obtaining 23,023 g of the composition of

the present invention.

Example 2

To the reaction vessel equipped with a stirrer were added 1,538 g of polyoxyethylenenonyl phenyl ether acrylate, 780 g of 2,4-tolylene diisocyanate, 4.0 g of dibutyl tin dilaurate, and 1.5 g of 2,6-di-t-butyl-4-methyl phenol, as a polymerization inhibitor, and 0.5 g of phenothiazine. After cooling the mixture over an ice water bath to 10°C, 600 g of 2-hydroxyethyl acrylate was added while maintaining the temperature at 30°C or less. After the addition, the mixture was stirred for one hour at 20-30°C. To the mixture were added 179 g of polyoxyethylene bisphenol A ether and 2,834 g polytetramethylene glycol with a number average molecular weight 2,000, while maintaining the temperature at 50°C or less. The reaction was terminated after stirring for a further 5 hours at 50-60°C, thus obtaining 5,937 g of a mixture of a polyol polyurethane (74 wt%) and polyoxyethylene nonyl phenyl ether acrylate (26 wt%) which is the reactive diluent. To the mixture were added 228 g of tricyclodecanedimethanol diacrylate as a reactive diluent, 2,890 g of trimethylolpropane ethoxy triacylate, 1,000 g of N-vinyl pyrrolidone, 150 g of Lucirin LR872 (manufactured by BASF) and 20 g of Irgacure 907 (manufactured by Ciba Geigy) as photopolymerization initiators. The mixture was stirred for 3 hours at 45 to 55°C thus obtaining 10225 g of the composition of the present invention.

Comparative Example 1

A composition was prepared in the same manner as in Example 2, except that no component (B) (trimethylolpropane ethoxy triacrylate) was added.

Comparative Example 2

A composition was prepared in the same manner as in Example 2, except that no component (C) (N-vinyl pyrrolidone) was added.

Evaluation of liquid curable resin compositions

The liquid curable resin compositions prepared in Examples 1-2 and Comparative Examples 1-2 were evaluated by measuring the viscosity of the compositions, the Young's modulus, breaking strength, and elongation at break of the cured products, and the adhesion strength with a ribbon material, according to the following methods.
The results are shown in Table 1.

Measurement of viscosity

The viscosity was measured at 25°C using a B-type viscometer manufactured by Tokyo Keiki Co., Ltd.

Evaluation of cured materials

1. Preparation of test specimens

The liquid curable resin compositions were applied to glass plates using an applicator bar to a thickness of 125 mm and irradiated with UV light at 0.1 J/cm^2 or 1.0 J/cm^2 using a jet printer HMW (manufactured by Orc Manufacturing Co., Ltd.) in a nitrogen atmosphere, to obtain cured films with a thickness of 50 μm. The films were peeled off from the glass plates and allowed to stand at 23°C and 50% RH for 24 hours. The resulting films were used as test specimens.

2. Measurement of Young's modulus

The test specimens were cut into stripes with a width of 6 mm to measure Young's modulus according to JIS K7113 at 23°C using Autograph AGS-1KND (manufactured by Shimazu Corp.), provided that conditions of a pulling rate of 1 mm/min and a pulling

stress at 2.5% strain were applied.

3. Calculation of the cure rate

The ratio of the Young's modulus of a film cured by irradiating UV light at 0.1 J/cm^2 and that at 1.0 J/cm^2 was calculated as the cure rate.

Measurement of strength and elongation at break of cured materials

1. Preparation of test specimens

The compositions were applied to glass plates using an applicator bar to a thickness of 300 μm and irradiated with UV light at 1.0 J/cm^2 in air to obtain cured films with a thickness of 200 μm. The films were peeled off from glass plates and allowed to stand at 23°C and 50% RH for 24 hours. The resulting films were used as test specimens.

2. Measurement of breaking elongation at break

The test specimens were cut into stripes with a width of 6 mm to measure breaking elongation at break at 23°C using Autograph AGS-1KND (manufactured by Shimazu Corp.), provided that conditions of a pulling rate of 1 mm/min and a bench mark distance of 25 mm were applied.

3. Measurement of breaking strength

The test specimens were cut into stripes with a width of 6 mm to measure breaking strength at 23°C using Autograph AGS-1KND (manufactured by Shimazu Corp.), provided that conditions of a pulling rate of 50 mm/min and a bench mark distance of 25 mm were applied.

Measurement of adhesion strength with ribbon a ribbon material

1. Preparation of test specimen

An optical fiber material (R3139 manufactured by Japan Synthetic Rubber Co., Ltd.) was applied to glass plates using an applicator bar to a thickness of 300 μm and irradiated with UV light at 0.5 J/cm² in a nitrogen atmosphere to obtain cured films with a thickness of 200 μm. The films were peeled off from the glass plates and allowed to stand at 23°C and 50% RH for 24 hours. The resulting films were used as the test specimens. The resin compositions prepared in the Examples and Comparative Examples were coated to one side of the test specimens using a spin coater (SPINNER 1H-2, manufactured by Mikasa Co., Ltd.) and irradiated with UV light at 0.1 J/cm² in a nitrogen atmosphere to obtain samples with a two layer structure, wherein the thickness of the resin compositions was 50 μm.

2. Measurement of adhesion strength with the ribbon material

The samples were cut into stripes with a width of 1 cm to measure the adhesion strength at a pulling rate of 50 mm/min using Autograph AGS-1KND Type I (manufactured by Shimazu Corp.).
The results are shown in Table 1.

TABLE 1

	Examples		Comparative Examples	
	1	2	1	2
Viscosity at 25°C (cps)	2000	1600	6000	2800
Curing rate Young's modulus (kg/mm^2) UV irradiation 0.1 (J/cm^2): a UV irradiation 1.0 (J/cm^2): b Curing rate: a/b	 16 22 0.73	 22 37 0.59	 22 29 0.76	 10 25 0.40
N-vinyl group/Acryloyl group*	0.40	0.30	0.92	0
Elongation at break (%)	17	29	120	32
Breaking strength (kg/mm^2)	1.6	2.8	2.9	2.6
Adhesion strength with ribbon material (g/cm)	60	57	30	85

* The ratio of the number of mols of the total N-vinyl groups and that of the total acryloyl groups in the resin composition. The closer is this ratio to 1.0, the higher is the degree of the alternate copolymerization of the N-vinyl groups and that the acryloyl groups and, therefore, the higher the curing rate.

The liquid curable resin composition of the present invention exhibits a high curing rate, provides high productivity in optical fiber manufacturing due to the low viscosity, and produces cured products with superior tearing characteristics due to the small extensibility. The resin composition is suitable for use as a bundling material and as a material for binding various other materials.

CLAIMS

1. A liquid curable resin composition comprising:
   (A) a polyol polyurethane containing an ethylenically unsaturated group,
   (B) a polyfunctional compound containing three or more (meth)acryloyl groups, and
   (C) a compound containing N-vinyl groups in a proportion of 0.25 to 2 mols for one mol of the (meth)acryloyl group contained in the composition.
2. The composition according to claim 1, wherein the polyol polyurethane contains a (meth)acrylate as unsaturated group.
3. The composition according to any one of claims 1-2, wherein component A has a weight average molecular weight of 500 to 20,000.
4. The composition according to any one of claims 1-3, wherein the composition contains 10-90 wt.% of component A relative to the total composition.
5. The composition according to any one of claims 1-4, wherein the composition contains 3-75 wt.% of polyfunctional compound containing three or more (meth)acryloyl groups.
6. The composition according to any one of claims 1-5, wherein the compound containing an N-vinyl group is N-vinyl caprolactam or N-vinylpyrrolidone.
7. The composition according to any one of claims 1-6, wherein the composition further comprises a photo polymerization initiator.
8. The composition according to any one of claims 1-7, wherein the composition further comprises at least one monomer having one or two (meth)acryloyl groups.
9. The composition according to claim 8, wherein the

composition comprises 1-80 wt.% of at least one monomer having one or two (meth)acryloyl groups.

10. The composition according to any one of claims 1-9 having a viscosity of 200-10,000 cps measured at 25°C.

11. Construction comprising at least two ribbons each ribbon comprising at least two coated optical glass fibers, the at least two ribbons are bound together by a bundling material wherein the bundling material is a cured composition, the composition before curing being the liquid curable resin composition according to any one of claims 1-10.

12. Construction according to claim 11, wherein the construction comprises 2-20 ribbons.

13. Construction according to any one of claims 11-12, wherein each ribbon comprises 2-20 coated optical glass fibers.

14. Construction according to any one of claims 11-13, wherein the coated optical glass fibers are color coated.

15. Construction according to any one of claims 11-14, wherein the bundling material has a Young's modulus of 5-50 kg/mm^2.

16. Construction according to any one of claims 11-15, wherein the bundling material has an Elongation at break of 3-70%.

17. Contruction according to any one of claims 11-16, wherein the bundling material has a breaking strength of 0.5-10 kg/mm^2.

18. Construction according to any one of claims 11-17, wherein the bundling material has an adhesion to the ribbon matrix material in the range of 5 to 200 g/cm.